Group 3 Dialkyl Complexes with Tetradentate (L, L, N, O; L = N, O, S) Monoanionic Ligands – Synthesis and Reactivity

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Supporting Information

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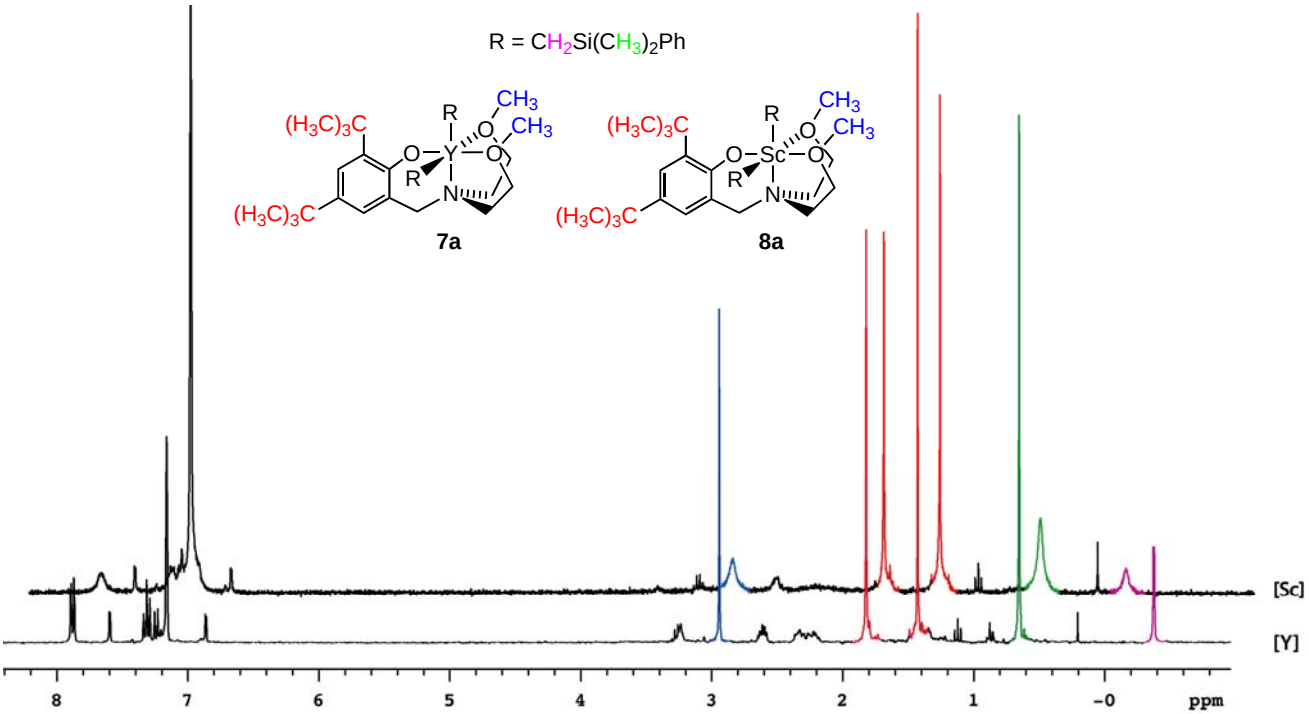


Figure 1. ^{1}H NMR spectra of **7a** and **8a** at room temperature.

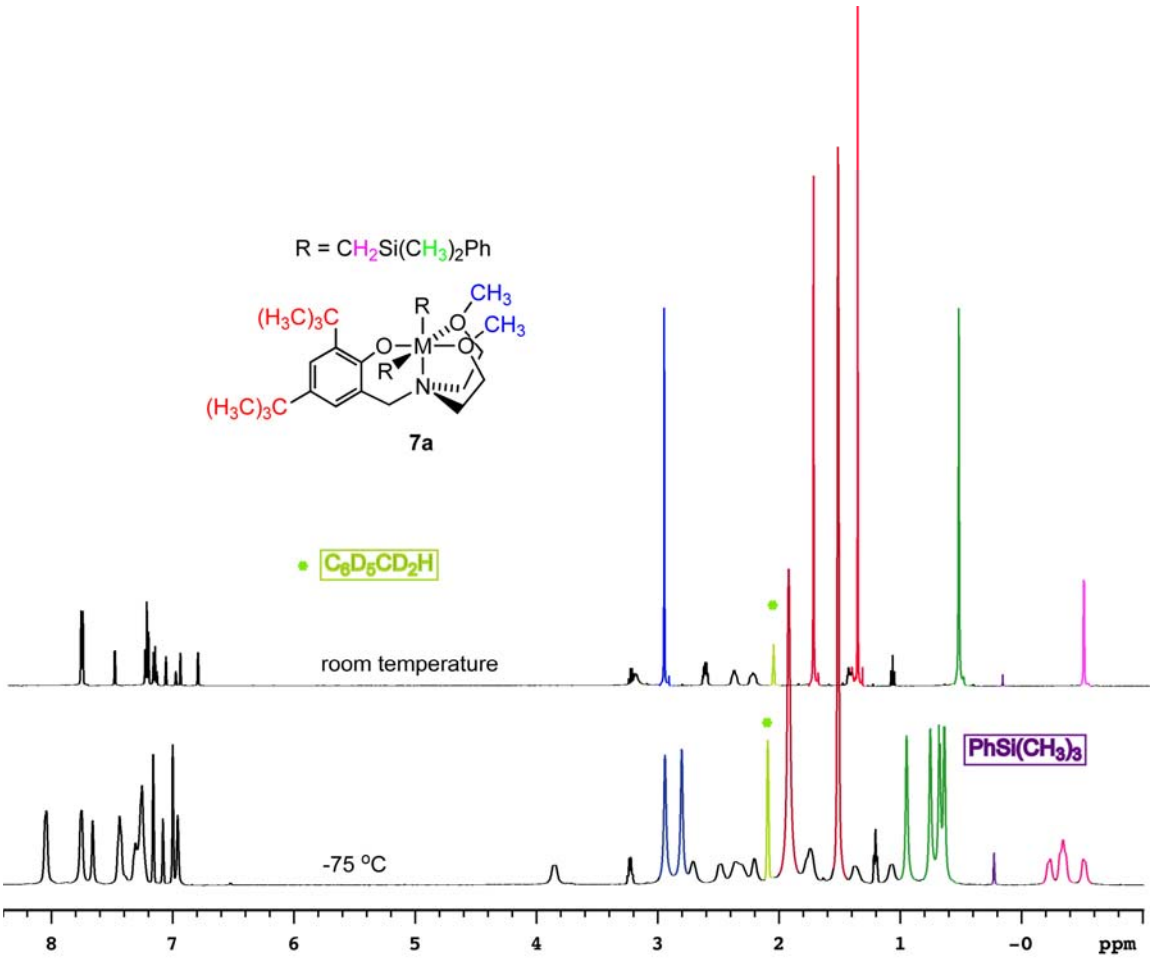


Figure 2. Variable temperature ^{1}H NMR spectroscopy studies of **7a**.

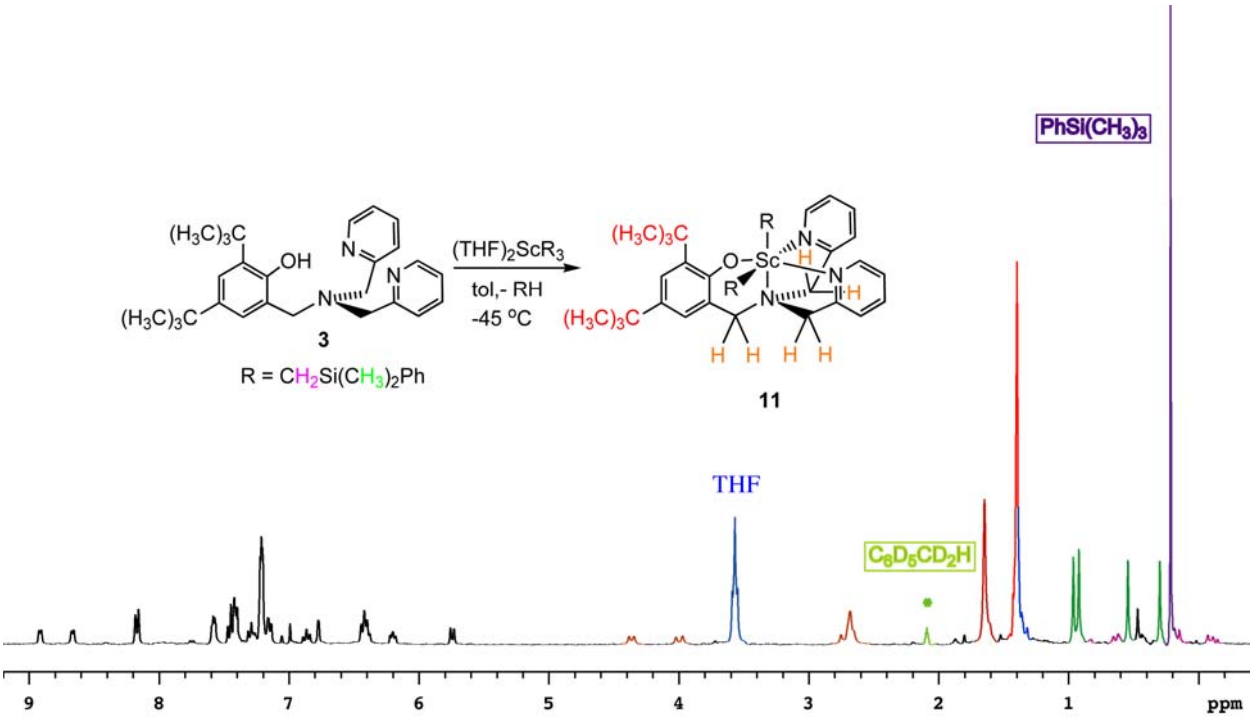


Figure 3. ^{1}H NMR spectrum of **11** at -45 ^{o}C.

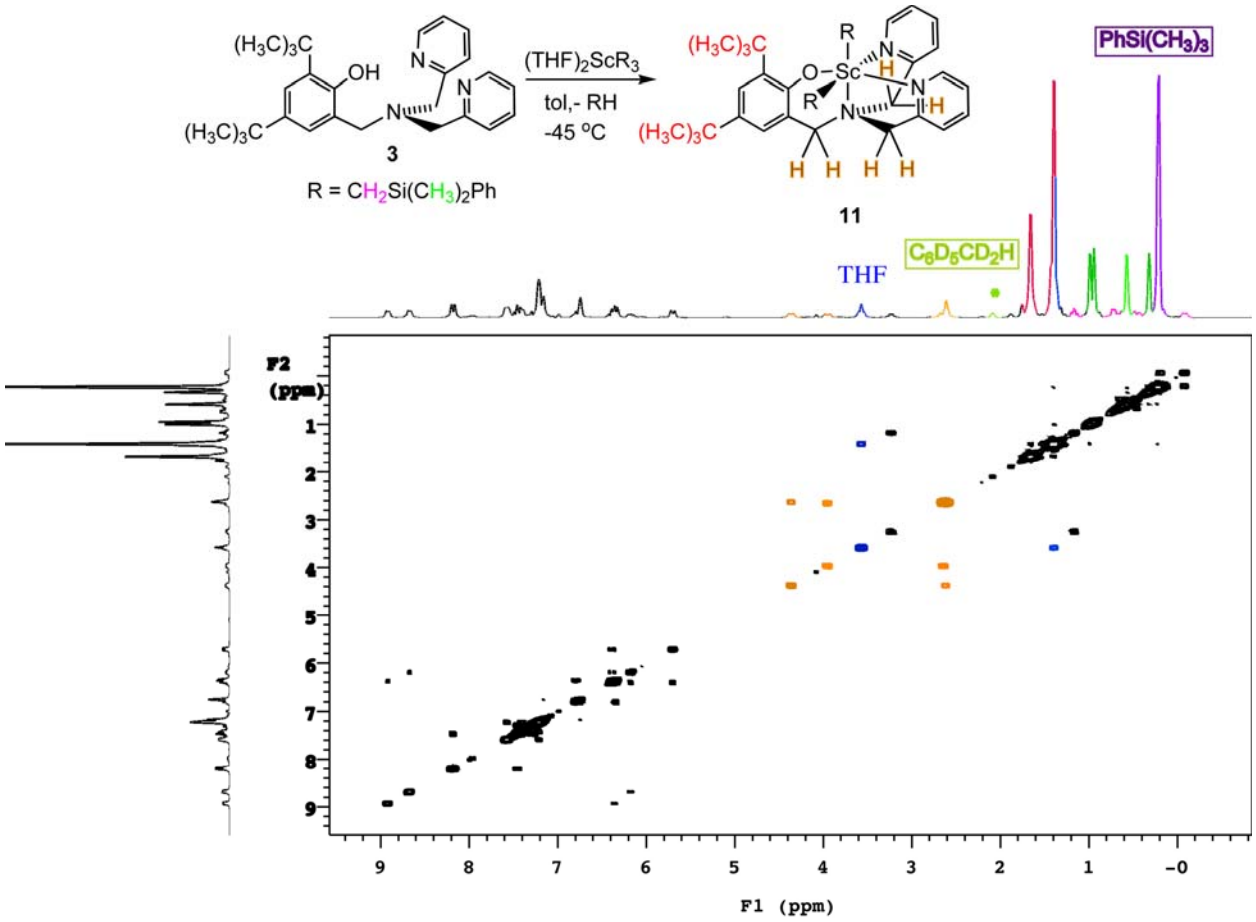


Figure 4. ^{1}H- ^{1}H COSY spectrum of **11** at -45 ^{o}C.

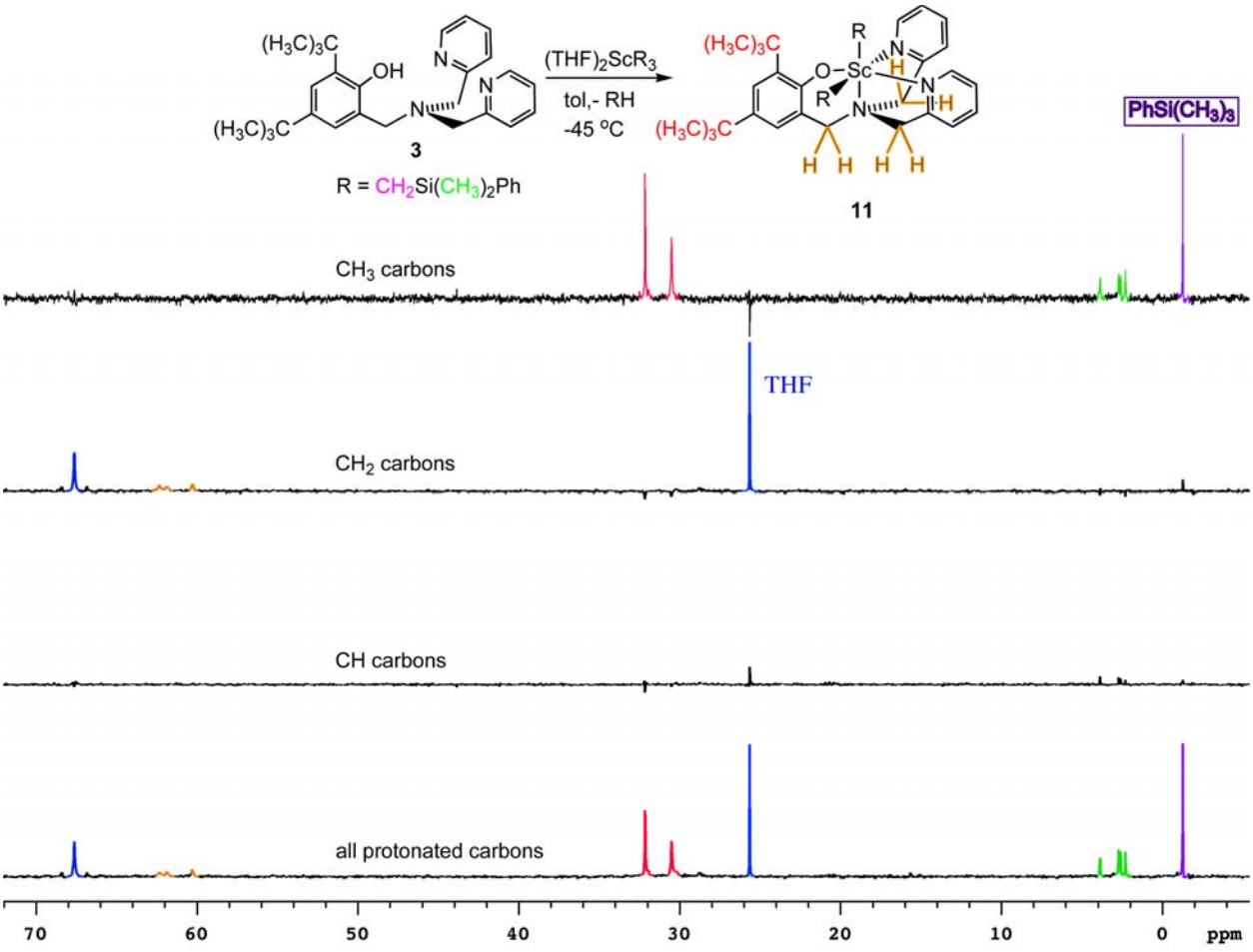


Figure 5. DEPT spectrum of **11** at -45 ^{o}C.

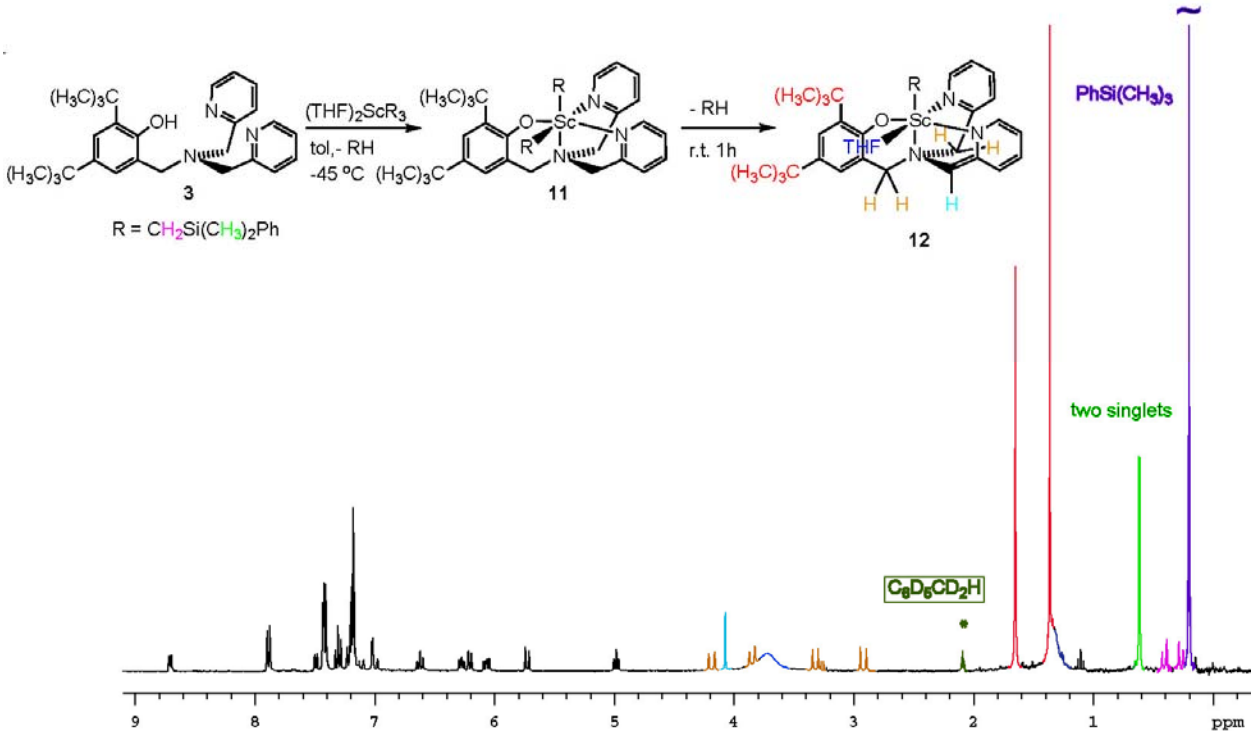


Figure 6. ^{1}H NMR spectrum of **12**.

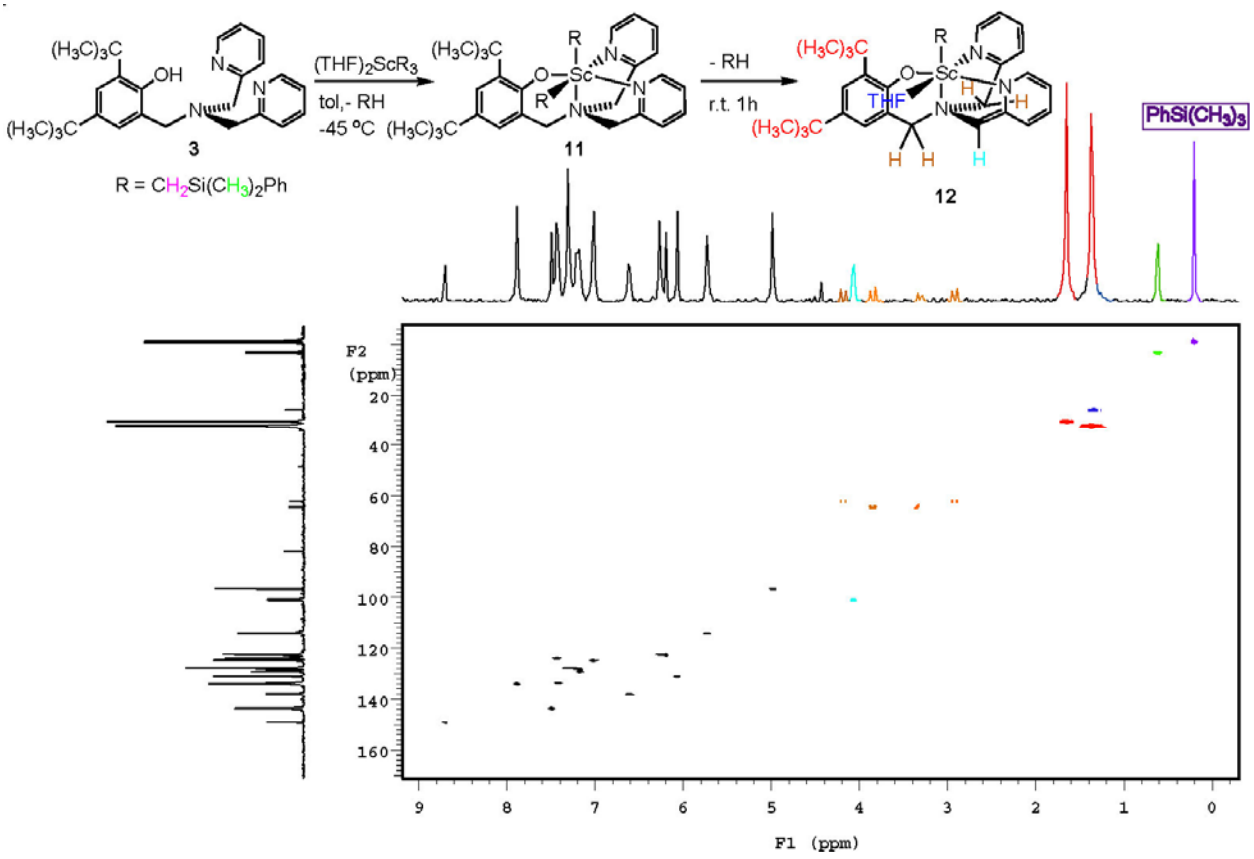


Figure 7. HETCOR spectrum of **12**.

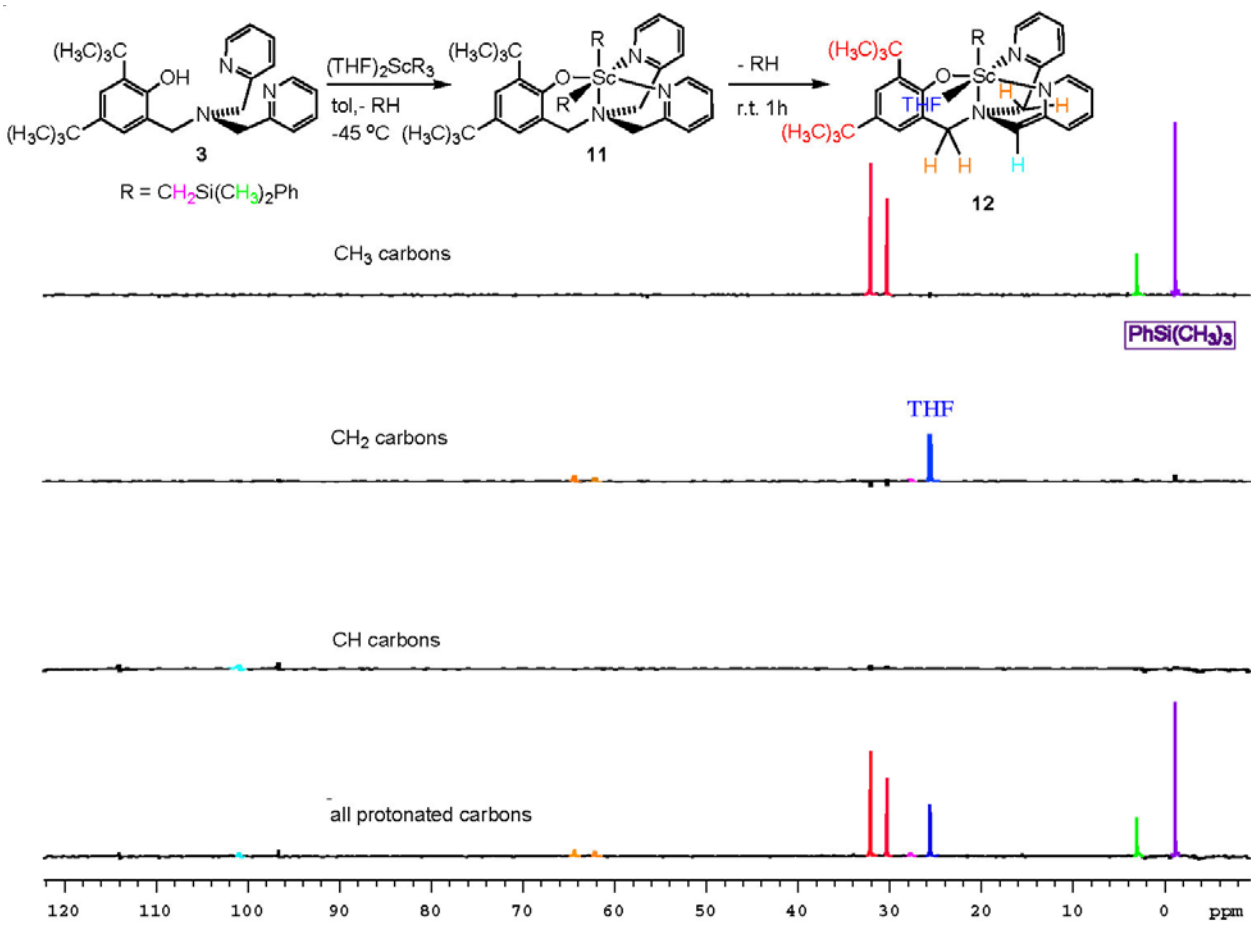


Figure 8. DEPT spectrum of **12**.

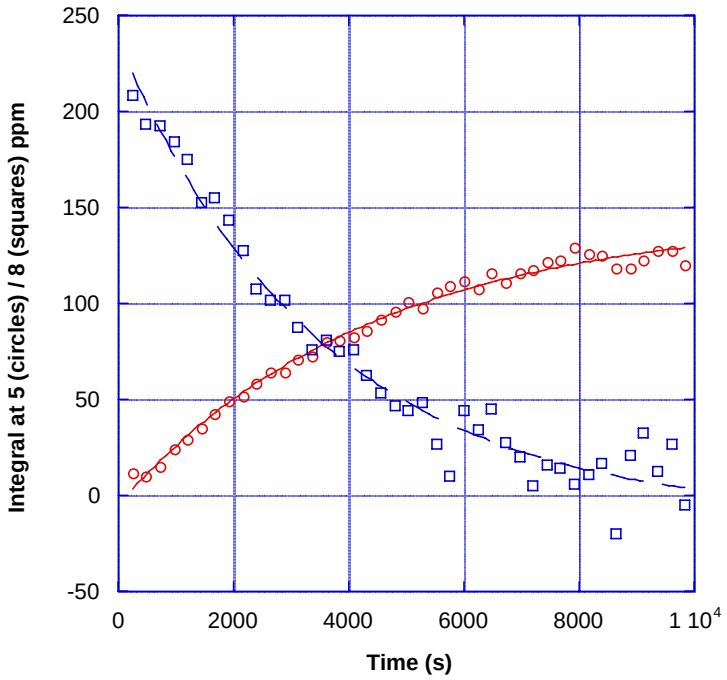


Figure 9. Kinetic studies of the conversion of **11** to **12** in toluene-d_8 at 0°C. Both the disappearance of **11** (blue squares) and the formation of **12** (red circles) were followed over time by measuring the integrals for baseline separated proton peaks at δ 8.08 ppm (2H), and δ 5.01 ppm (1H), respectively. Equation used: $y = I_f + (I_i - I_f)\exp(-kt)$.

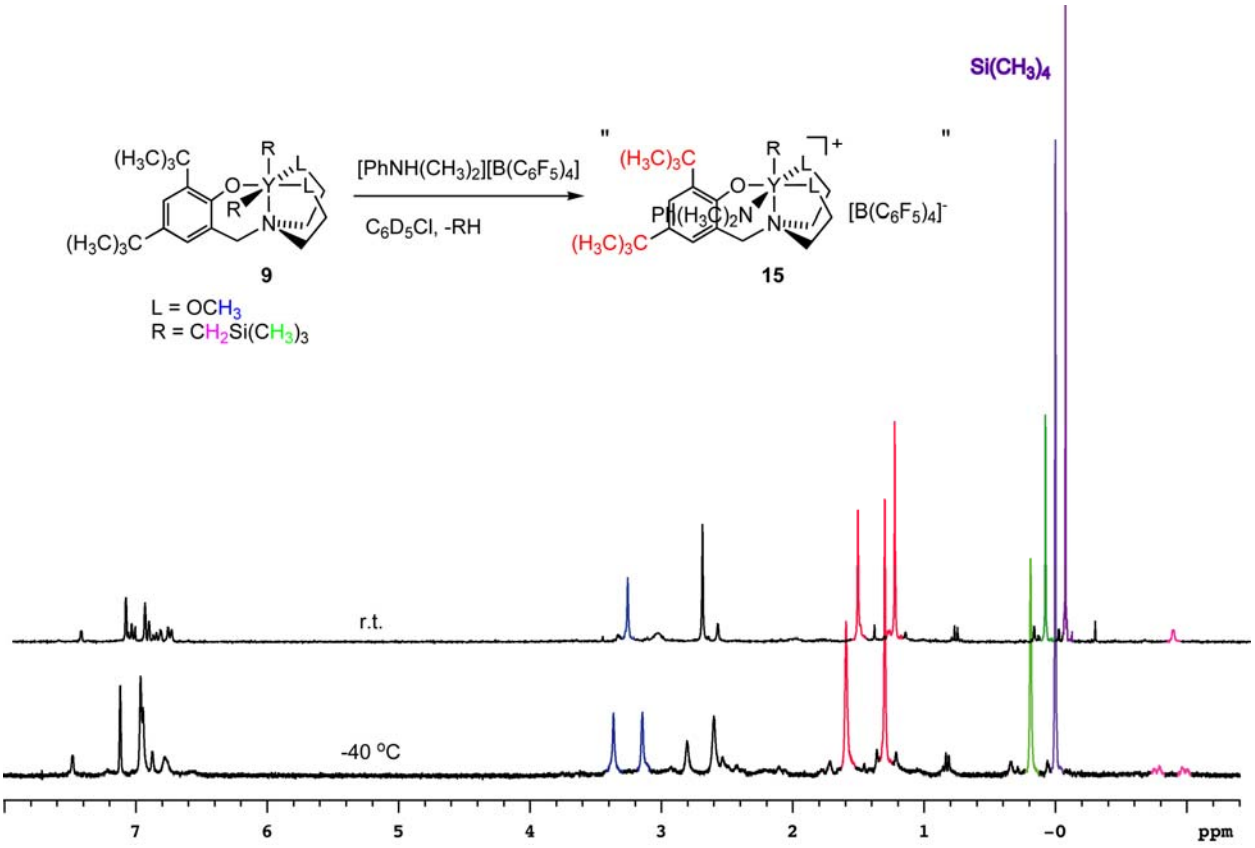


Figure 10. ^{1}H NMR spectroscopy studies of **15**.

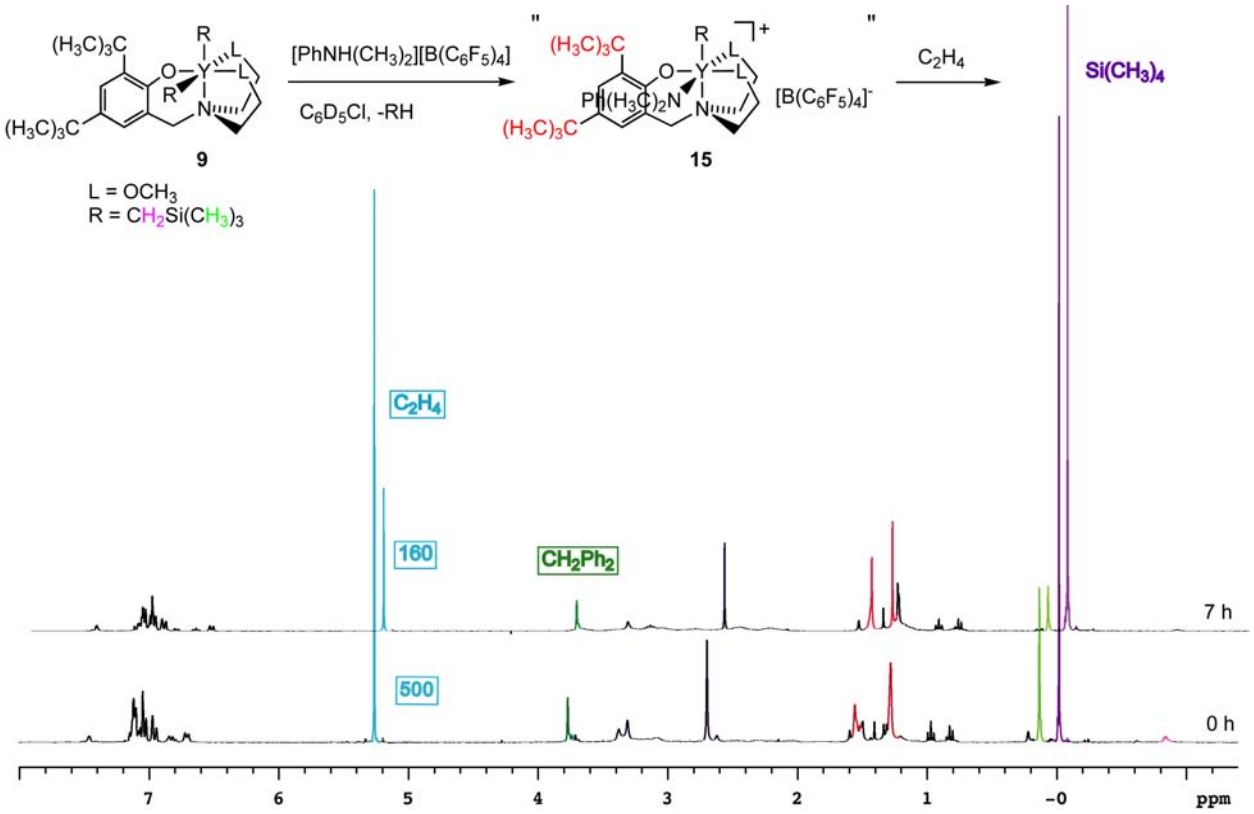
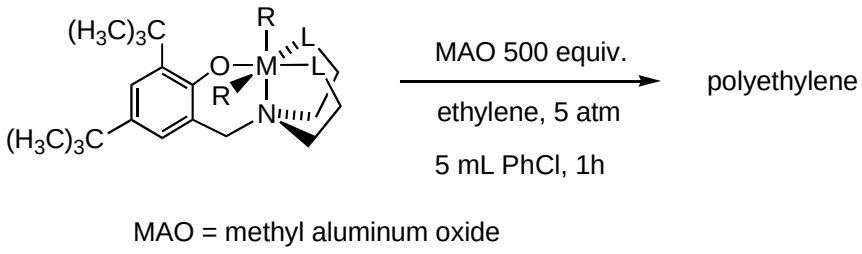


Figure 11. ^{1}H NMR spectroscopy studies of **15** in the presence of ethylene.



MAO = methyl aluminum oxide

No.	Compound	Productivity (Kg PE·mol M^{-1}·h^{-1}·bar^{-1})	
1	M = Y, L = OCH_3, R = $CH_2Si(CH_3)_2Ph$ (**7a**)	1.4	2.0
2	M = Y, L = NEt_2, R = $CH_2Si(CH_3)_2Ph$ (**7b**)	1.1	0.9
3	M = Sc, L = OCH_3, R = $CH_2Si(CH_3)_2Ph$ (**8a**)	0.9	0.8
4	M = Sc, L = $SCMe_3$, R = $CH_2Si(CH_3)_2Ph$ (**8b**)	2.5	2.5
5	M = Y, L = OCH_3, R = $CH_2Si(CH_3)_3$ (**9**)	0.9	1.0
6	M = Sc, L = OCH_3, R = $CH_2Si(CH_3)_3$ (**10**)	1.3	0.6

Table 1. Polymerization trials of the metal dialkyl complexes. Conditions: 1.67 μmol catalyst, 500 equiv. MAO, 5 mL solvent (chlorobenzene), 5 bar, 1 h.

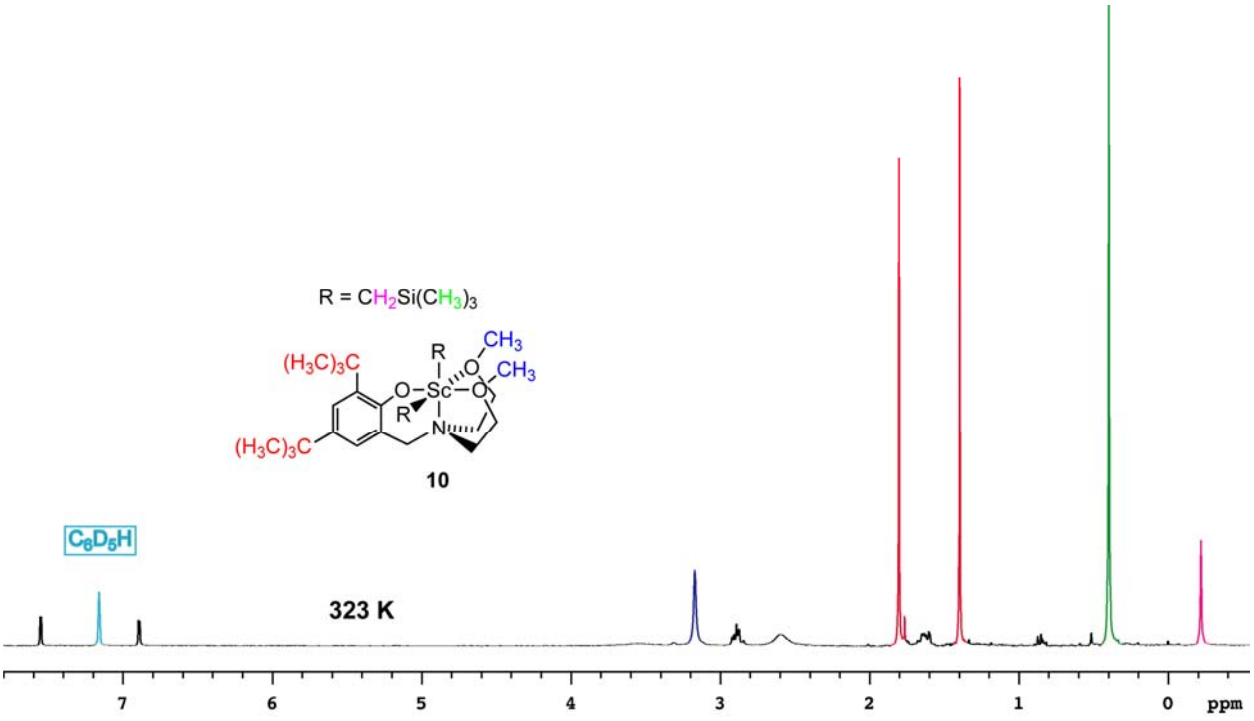


Figure 12. ^{1}H NMR spectrum of **10**.

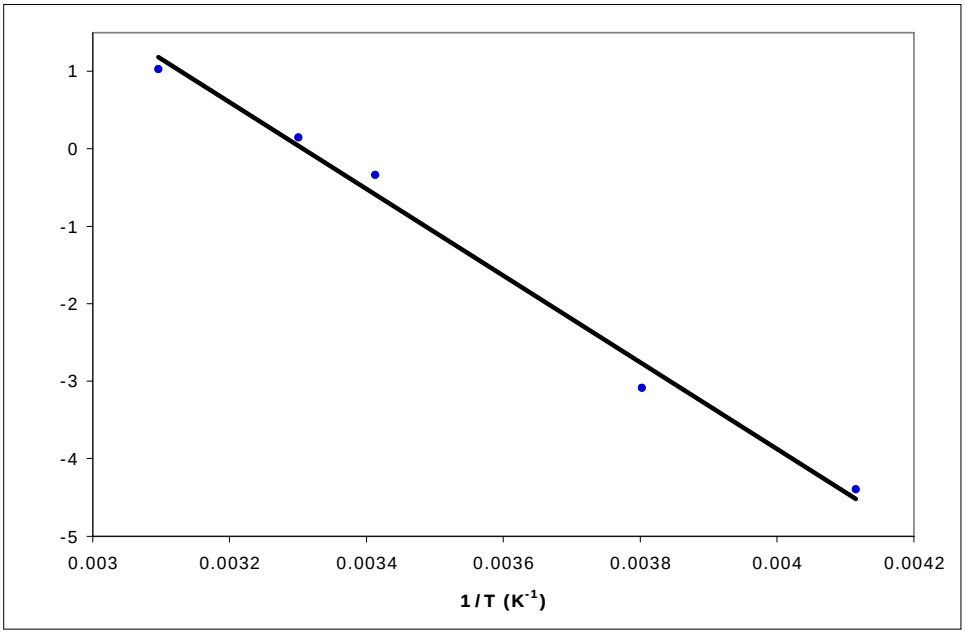


Figure 13. Eyring plot for Si(CH_3)$_3$ in **10** (toluene-d_8, 300 MHz).

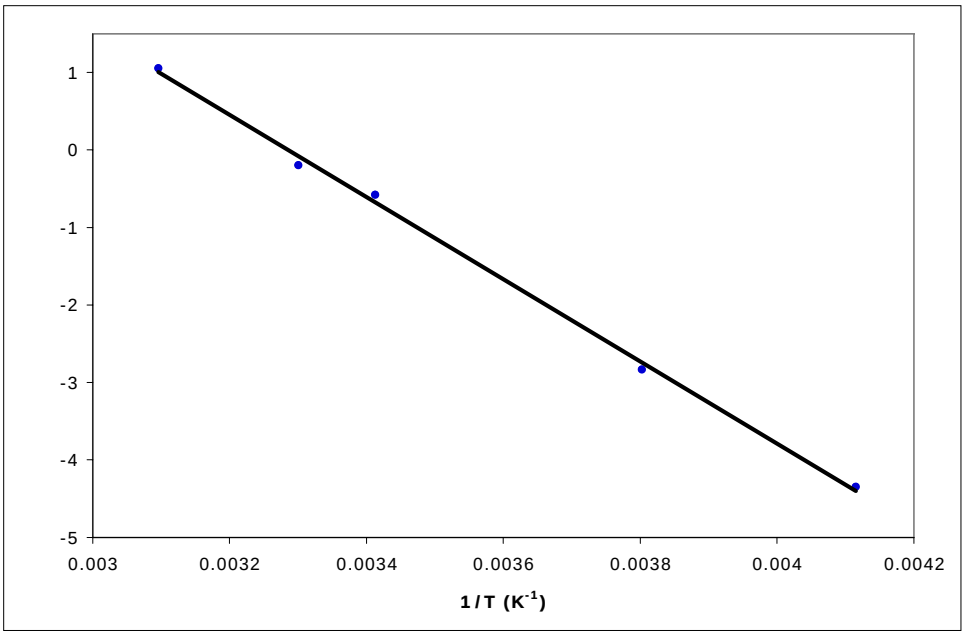


Figure 14. Eyring plot for OCH_3 in **10** (toluene-d_8, 300 MHz).